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Cleaning Method for VLF Cooling Water System Development and History of Application with Step-by-Step Procedure

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13. ABSTRACT (Maximum 200 words) In 1980 NRL Chemistry Division personnel analyzed a black solid forming on the walls of VLF transmitter tubes that was lowering the flow rates of the cooling water. Chemical analysis of the black solid showed it to be copper (II) oxide, CuO. This result implied uncontrolled corrosion in these systems, and it was apparent that the following efforts were needed: (1) evaluation of the corrosion processes causing the formation of this product; (2) design of a chemical cleaning approach to remove this solid; (3) development of methods to inhibit or slow the formation of the CuO. This report documents procedures used to clean the VLF water cooling systems and transmitter tubes.				
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CLEANING METHOD FOR VLF COOLING WATER SYSTEM DEVELOPMENT AND HISTORY OF APPLICATION WITH STEP- BY -STEP PROCEDURE

FORWARD

This memorandum report contains information from several letter reports that were written in the 1980's and 1990 concerning the development of the cleaning and maintenance procedures for the water-cooled VLF sites. It was suggested that they be edited and organized into one document for ease of use and historical record. Historically, letter reports are archived for five years and then disposed while memorandum reports are held indefinitely. The work that is detailed in this memorandum report is the result of efforts by Drs. J. Cooper, A. Ervin, and K. Hardy.

In order to maintain copper oxide free (or nearly free) water cooling systems, all the water cooled VLF sites now have Nitrogen sparging systems to maintain the concentration of dissolved oxygen in the cooling water to below 0.5 ppm. It is very important that once a cleaning has been accomplished, the dissolved oxygen concentration in the cooling water be monitored to ensure that it is below the 0.5 ppm permissible level. To effect this, dissolved oxygen sensors have been installed at all the water cooled VLF sites. Both the nitrogen and dissolved oxygen systems are low maintenance systems that reduce the failure rate of power amplifier (PA) tubes due to overheating by the accumulation of copper oxide on the surfaces of the PA tubes.

INTRODUCTION

In 1980 NRL Chemistry Division personnel analyzed a black solid forming on the walls of VLF transmitter tubes that was lowering the flow rates of the cooling water. Chemical analysis of the black solid showed it to be copper (II) oxide, CuO. This result implied uncontrolled corrosion in these systems, and it was apparent that the following efforts were needed: (1) evaluation of the corrosion processes causing the formation of this product; (2) design of a chemical cleaning approach to remove this solid; (3) development of methods to inhibit or slow the formation of the CuO.

THE COOLING SYSTEM

The high power levels in the final amplification stage of Naval VLF transmitters make use of vacuum tube technology. The vacuum tubes generate 150 to 250 kilowatts of R.F. output power each and produce a similar amount of heat which must be removed to prevent tube failure. Circulating water is the preferred method of cooling the tubes at Naval VLF sites; water is an excellent coolant due to its chemical stability and its large heat transfer capabilities. While air can sometimes be used as a coolant, it is not used in warmer climates where input air temperature is high, nor is it used where high output

power is needed. The principal metal and plumbing material in the system, copper (also known for its excellent heat transfer properties) is used in the transmitter tubes and for the plumbing of the cooling loop. The temperature at the surface of the tubes must be maintained at less than 300° C, and the maximum specified temperature for the ceramic/metal seal is 200 ° C. Most systems operate so that the effluent water from the transmitter tubes is kept at 50-60 ° C. The actual temperatures at the tube surfaces are uncertain but there have been cases of sufficient localized heating where anode surfaces were coated with copper oxide to collapse the vacuum tube.

The configuration of the cooling system is shown in Figure 1, and will be discussed in more detail below. The cooling water is stored in a surge/reservoir tank usually made of stainless steel. From there it is pumped into copper pipes and the flow is divided into individual pathways [1] for each pair of transmitter tubes. Inside the tubes, the flow is also divided into two pathways, one for the anode, where most of the heat is generated, and the other path for the rest of the tube. Since the anode is normally at high potential to ground, the water connections to the anode are made through insulating tubing made of ceramic. The coolant for the anode is further divided into smaller pathways arranged around the cylindrical periphery of the tube. The subdivisions in these pathways can be as small as .025 inches. After flowing through the tubes the water is combined and taken back to the main cooling loop where it is passed through a heat exchanger, usually made of copper, and then back into the surge tank. Other materials are also used where copper does not have the structural strength needed such as for valves, pumps and welded structure. Suggested materials, chosen to avoid or minimize galvanic action are nickel, bronze, Monel, Inconel, 304L stainless and 347 stainless. Materials to be avoided are steel, cast iron, galvanized iron, aluminum and magnesium. Thus, stainless steel is used for the surge tanks and in the pumps. The transmitter tubes have ceramic tubes making cooling water connections to the anode. The pumps have all-brass internals and various valves are made of brass, bronze and stainless steel.

Water flow rate is varied to maintain sufficient cooling capacity. The pumps vary among the VLF sites; the range in output flow rates is 60-180 gpm. Associated with the water cooling loop are various monitors for flow rate, temperature and pressure at the input and output sides for each transmitter tube. The flow rate specified by one tube manufacturer [2] for a 150 kW tube is 37.5 gpm and for a 250 kW tube it is 60.0 gpm. The typical input temperature is 50° C and the outlet temperature should not exceed 70° C. The pressure drop from the input to output side is also specified, 3.5 psi for 150 kW and 10.0 psi for 250 kW. These specifications are well within safe limits for heating of the tube but they do not mean that the temperature is constant throughout the system. Heat fluxes do occur and the formation of any solid precipitate on the tube walls can lead to reduced water flow, especially if the small tubes are plugged or hot spots result, which can shorten tube life.

SPECIAL NEEDS OF THE COOLING SYSTEM

Although copper is an excellent heat transfer material and water is an excellent coolant, having them in contact can lead to problems. Most problems with the cooling system relate to heat fluxes and to the build up of precipitates in the cooling loop. The solids formed are of two kinds, scale and corrosion products. Scale is caused by the

presence of ions in the water at high enough concentration to precipitate salts on the tube walls and throughout the cooling system. The corrosion products result from oxidation of the copper. Both solids are thermally insulating and both precipitate on the vacuum tubes decreasing heat transfer and causing hot spots. In addition, they plug the cooling tubes and decrease flow rates and heat dissipation. This decrease in heat removal compromises the Naval VLF communication system by tube failure and system shut-down.

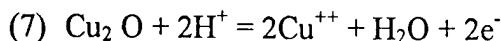
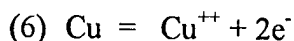
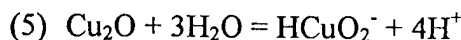
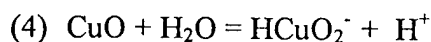
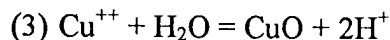
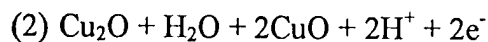
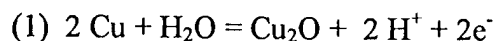
Prevention methods are utilized to avoid corrosion products and scale on the tube walls. Scale formation is successfully decreased by maintaining water at resistivity $>200 \text{ K}\Omega\text{-cm}$. Make-up and feed water are prepared with a high quality water still. Whenever the conductivity becomes too high, the cooling water is cycled through a purification loop consisting of ion exchange columns until the output water resistivity is $>200 \text{ K}\Omega\text{-cm}$. These techniques remove ions that can precipitate on the tube walls as scale.

Control of oxidation is somewhat more difficult. The fact that oxidation does occur was demonstrated by identification of copper(II) oxide, CuO , on the tube walls. Black solids which slowed the flow of cooling water were collected from tube walls and the purification loop at Jim Creek and Annapolis. The solids collected at these sites were found to be 56% copper and less than 0.5% each iron, zinc and lead. Auger spectroscopy showed the oxidation state of copper to be (II) [3].

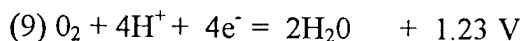
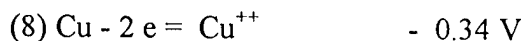
There are two faradaic routes of CuO formation available: (1) the spontaneous galvanic reaction of oxygen dissolved in the water with the copper of the tube walls, and (2) the electrolytic reaction driven by the potential difference between the cathode and the anode of the vacuum tube. A useful tool in understanding oxidation processes are Pourbaix diagrams [4-6]. These will be used to look at galvanic oxidation. The diagram for pure water is shown in Figure 2. Lines a and b represent the reactions (a) and (b) and are obtained by plotting the potential as a function of pH using the potential-pH equations shown with the reactions. These are for standard conditions of temperature, 25°C , and 1 atm pressure for oxygen and hydrogen. In the region between the lines in Figure 2, water is thermodynamically stable. Below curve a, water is unstable with the release of



hydrogen and alkalization of the media. Above curve b, water is thermodynamically unstable to the formation of oxygen and acidification. At the conditions of the cooling water, pH 6- 7, with no added potential, no decomposition of the water is expected. The Pourbaix diagram [4] for copper is plotted along with the diagram for water in Figure 3. This plot represents copper in pure water which is the condition for the transmitter tube in water with no added species. The reactions used to produce this diagram are given here and the numbers on the curves relate to the reactions. All ions are aqueous and all uncharged copper species are solids.



The curves can now be used to determine which species is most stable for certain conditions of pH and potential. For example, to the left of curve 3, $\text{Cu}^{++}(\text{aq})$ is the stable form of copper and to the right $\text{CuO}(\text{s})$ is the favored species. Regions of the plot have been labeled with the thermodynamically favored species. Using this diagram for the conditions of the copper of the VLF transmitter tube in pure water and with no applied potential, it is apparent that the copper is thermodynamically stable to corrosion. However this stability is lost by the presence of any added materials. For example, if oxygen is present there is sufficient driving force to shift the curve upwards. The two half reactions (6) and b, rewritten here as (8) and (9) form a couple with a



potential difference of 0.9 V so that if O_2 is present in the water the copper will oxidize. Looking at the Pourbaix diagram in Figure 3 at $E = 0.9 \text{ V}$ and $\text{pH} = 6-7$, it is possible to predict that reaction 3 will proceed, forming $\text{CuO}(\text{s})$ as a final product. So, although copper is very stable to corrosion in pure water, it corrodes in air saturated water.

To evaluate the contribution of this process at the VLF sites the concentration of oxygen in the cooling water was measured at Jim Creek [7,8]. The values found, 4-6 ppm, are expected for air saturated water and make the oxidation of copper and the formation of $\text{CuO}(\text{s})$ by the galvanic process described above the reasonable explanation for the formation of the black solid on the tube walls. At the time these measurements were made, the purification loop included "oxygen removal cartridges". Examination of these cartridges revealed problems. First, they had inadequate capacity for their application. They were rated for 10-15 g of oxygen. A new start up at Jim Creek would require the removal of 65 g of dissolved oxygen, or seven cartridges. Oxygen incursion [9] experiments were then done at Annapolis to determine the cartridge requirements for normal conditions. After reducing the oxygen level to 2.5 ppm by sparging with nitrogen, the sparge was discontinued, the water continued to circulate and oxygen levels were measured over time. Oxygen entered the system at the rate of 10 g/hr and the system quickly reached air saturation. Air entry is probably through leaky pump seals and quick-

connect fittings and is probably impossible to avoid without different types of circulating pumps and extensive redesign. The use of these "oxygen removal cartridges" at this incursion rate would require a new one every hour. The cartridges in use were clearly not adequate [9].

Another problem also became apparent from the study of these cartridges; they release amines into the cooling water system [3]. Pourbaix diagrams [6] are again useful to understand the effect of adding a complexing agent into the water as in Figure 4. Ammonia reacts with both copper(I) and copper (II) to form stable complexes. This affects the equilibria by stabilizing the oxidized form and driving the reaction of more copper oxidation. Ammonia also raises the pH and it dissolves CuO [4] making fresh copper metal surfaces available for corrosion. It has been estimated that amines increase the amount of oxidation by 1-2 orders of magnitude. Any complexing agent in the water will have this effect. Even chlorine or hypochlorite which may be in the water from the source water treatment, can be reduced to chloride, and act as a ligand stabilizing the oxidation products.

These reactions proceed with no external input of energy, i.e., they are spontaneous. For this system it is also necessary to consider the possibility of the electrolytic oxidation of copper driven by the potential difference between the cathode and the anode of the vacuum tube. Considering only faradaic processes it is possible to calculate the amount of copper electrolysis expected. According to tube specifications [2] the plate voltage (E) is 13.0 kV for the small tubes. The water path length (l) from the anode to ground through the ceramic cooling tubes is 660 cm, and the cross sectional area (A) of the path is 1 cm². The resistance (R) in ohms (Ω) can be calculated using equation (10)

$$(10) R = \rho \times l / A$$

where ρ is the resistivity in Ω -cm. Current, i, in amps or coulombs/sec (C/sec) is then calculated using equation (11)

$$(11) i = E/R$$

where E is the potential in volts and R is the resistance in Ω as calculated in equation (10). From the current it is then possible to calculate the grams of copper released using equation (12) and assuming all the electrons react with copper in the electrolytic oxidation.

$$(12) \text{ Cu(g/yr)} = i(\text{C/sec}) \times 31,536,000 \text{ sec/yr} \times 63.5 \text{ g Cu/mole Cu} \times 1 \text{ mole } e^- / 96,487 \text{ C} \times 1 \text{ mole Cu/l moles } e^-$$

Using different resistivity values it is possible to evaluate the amount of copper oxidation expected for "good" and "bad" water. The recommended water resistivity is greater than 200 k Ω -cm. Calculating the amount of copper oxidized in water of varying resistivities, it is found that in water with resistivity of 1 M Ω -cm, 0.4 g of copper will be oxidized in one year. If the water quality goes down to 200 k Ω -cm. the point at which the purification loop must be used, there will be 2 g of copper oxidized in one year.

In water with good resistivity control, the contribution of electrolysis is low and insignificant compared to air-oxidation. It was therefore important to develop a new way to control the oxygen levels in the cooling water. Varian [1], one of the tube manufacturers, recommends that the O₂ concentration be maintained at less than 1.25%. NRL demonstrated the efficacy of nitrogen purge as a method of controlling corrosion [10] using bottled nitrogen and has since implemented and tested a more permanent purge system using nitrogen separated from air at Lualualei [11]. The overall project of corrosion prevention using nitrogen purge is summarized.

HISTORICAL-DEVELOPMENT OF A CLEANING METHOD

Given the level of corrosion in the system it was essential to clean the cooling system and to remove the copper(II) oxide. Varian product literature includes directions for removing the tube from its holder and cleaning it with dilute hydrochloric acid. However, at the VLF sites it was necessary to clean the total cooling loop without dismantling the plumbing. Therefore a chemical cleaning which does not damage any of the system components is the best option. Four cleaning methods [13, 14] described in the literature are described here:

1. Inhibited Hydrochloric Acid

Dilute hydrochloric acid is used with an inhibitor to reduce attack to metal surfaces. This method was used at Jim Creek (but not in the tubes) in 1958. The method is inexpensive; but handling hydrochloric acid in large volumes is risky to personnel. And the inhibitors do not protect brass and zinc components.

2. Citric acid/EDTA

In this combination the citric acid acts to dissolve a metal oxide and the EDTA sequesters the metal ions keeping them in solution. Although it is a very effective method the disposal of EDTA is not trivial. The method of choice is incineration to yield carbon dioxide, water and nitrogen oxides. The flue of the incinerator must be equipped to scrub the metals and the nitrogen oxides from the gas. Another time consuming method is to use sewage treatment facilities. Because of the volumes of solutions needed and the remote locations of the sites this alternative is not attractive.

3. Radiator Cleaning Preparations

The second approach recommended by Varian is the use of a commercial preparation designed to flush an automobile radiator. Difficulties that accompany use of these are corrosion of the system components while the copper oxide is dissolved and the fact that they are a mixture of proprietary and therefore unknown components. This only complicates the selection of sound environmental disposal methods.

4. Ammoniated Citric Acid

A solution of 10% citric acid with ammonia added to raise the pH and to sequester copper in solution is one of two methods recommended by the manufacturer [3] of the 4CW250.000B tubes. Because of the usefulness of this method, some laboratory pretests were done and some potential problems were identified. In air saturated systems with ammoniated citric acid it was found experimentally that the rate of copper corrosion is greater than the rate of copper oxide dissolution [3]. To circumvent this problem an oxidation inhibitor, erythorbic acid (iso-ascorbic acid) was added to the solution. The addition of this antioxidant and reducing agent makes it possible to dissolve the copper oxide without concomitant risk of damage to critical brass and copper components. This mixture has the added benefit that it is safe to handle and environmentally innocuous. By mixing citric acid and ammonium citrate, a solution with pH 3-4 can be attained and there are no problems with ammonia vapors. Both citric acid and erythorbic acid are components of food, the latter being used as an antioxidant and preservative. Both are non-toxic. The disposal problem is also easier with this mixture. The only disposal issue is the slightly low pH, which can be corrected by neutralization with sodium bicarbonate. The solution can then be treated by a municipal sewage facility, and if the copper concentration is low enough it can be discharged onto the ground.

CHOICE OF THE METHOD

Of these four options, it was decided to use the ammoniated citrate solution modified on the basis of the laboratory pretests by the addition of erythorbic acid. The concentration (w/w%) of the solution was chosen to be 1.5% citric acid, 1.8% dibasic ammonium citrate plus enough more to bring the pH to 3.5-4 (for a total citrate concentration of about 3.3%), and 1-2% erythorbic acid. The water was to be heated to 60° C. If the cleaning did not proceed quickly enough due to thick layers of oxide, several options are available: 1. the temperature could be raised; 2. the concentration of the citrate could be increased and/or; 3. the amount of erythorbic acid could be increased. On the other hand, if elemental copper (red in color) were to form in the cooling water due to reduction by erythorbic acid, it would be necessary to flush the system to avoid plugging with copper solids and to then use less erythorbic acid. This method was chosen because it was deemed the most efficient, the safest in terms of toxicity, the easiest to dispose and it was possible to adapt it to minimize additional corrosion caused by the cleaning.

HISTORICAL- SYSTEMS CLEANED AND PROBLEMS FOUND

Since this cleaning method was first developed it has been used five times: Jim Creek in July of 1980; H.E. Holt in November of 1981; Lualualei in January of 1982; Annapolis in August of 1986; and Lualualei in April of 1989. Each site cleaning will be described here with special attention given to the problems that developed. The next section of this report will give a more detailed step-by-step description of how to do a cleaning. The Jim Creek VLF site was the first cleaned. After a site visit in May 1980 [8], initial laboratory analyses [7], and a laboratory refinement of the cleaning method chosen [3], the cooling water system was cleaned in July 1980. The cleaning and restart took 4

days. The cooling system at Jim Creek is a tandem system with two, one thousand gallon surge/reservoir tanks; the total volume of the two tanks and the plumbing is about 2800 gallons. Initially it was planned that the two sides would be cleaned separately necessitating removal of the main union between them. This was not done; rather one tank was used for the entire system cleaning of both sides and the other tank was cleaned by itself. In the system cleaning, 600 gallons of water with 1.5% citric acid, 1.75% dibasic ammonium citrate, and 2% erythorbic acid were circulated for 40 minutes, at which time a red solid formed (elemental copper). The cleaning solution was quickly pumped into a holding tank and the system was rinsed, drained, and flushed again. After draining and refilling a second cleaning was done using only 1.2% citric acid, and 1.3% diammonium citrate in solution. This mixture was circulated for one hour and twenty minutes, until the copper concentration stayed constant. The system was then rinsed, dumped, refilled, circulated over night and dumped. The rinse was repeated using good quality water (resistivity, $\rho = 600 \text{ K}\Omega\text{-cm}$) until the inlet water measured $450 \text{ K}\Omega\text{-cm}$. The other tank was cleaned with 1.2% citric acid, and 1.4% diammonium citrate solution and it too was rinsed until its water quality was good. The much greater coating of copper oxide on the tubing compared to the plumbing required that the tubes be removed and cleaned individually by hand.

The next station to be cleaned was H. E. Holt. A site visit was conducted in February of 1981 [5] and the cleaning was done in November of 1981. The actual cleaning took 3 days. Here each cooling loop was cleaned separately; there are 4 PA's and 2 IPAs at this site. One problem was encountered at this site: the lack of a drainage valve on each tank. It was necessary to install one and move it to each subsequent tank. A diesel powered portable pump was used to pump fresh water. The chemicals were mixed separately for each loop (1.5% citric acid, 1.75% dibasic ammonium 2% erythorbic acid). Initially, for PA1, the cleaning was begun with the tubes out, but for the rest they were left in for several minutes, until examined and found to be clean. At this time they were removed and plugs were inserted for the rest of the cleaning and the circulation of rinse water. Three of these loops developed some (red) elemental copper during circulation of the cleaning chemicals: the solutions were quickly drained and the rinsing begun. Also at this site three (one of those with elemental copper and two without) of the tanks showed substantial amounts of sludge formation. The first time this happened the pump was clogged and stopped working. In all cases the sludge was manually removed by wiping it out of the tanks.

The third site, Lualualei, was cleaned shortly after H. E. Holt in January 1982, and was recleaned in April 1989 [11]. Before the cleaning in 1982, two site visits had been made, January 1981 and October 1981 in route to H. E. Holt. The first cleaning required 3 days. The concentrations used were the same as those for H. E. Holt. In this cleaning the IPAs were cleaned without incident; IPA1 required three distilled water rinses and IPA2 required four. The tubes were left in place and cleaned with the cooling system; they were inspected during the cleaning and removed when they looked clean. To clean the Pas, a bypass was inserted around the heat exchangers because they were very fragile (corroded, thin wall tubes) and were about to be replaced. The bypass consisted of fire hoses reduced in size such that the PA pumps (120 gpm) caused the fire hoses to be blown off. To circumvent this problem the PA's were cleaned together (in parallel) using only one pump. The tubes were cleaned *in situ* and then removed. Three distilled water

rinses were required before the system could be put back on the purification loop.

The second cleaning at Lualualei was conducted in April of 1989 [11], after a site visit in January of 1989. The tubes were removed for this cleaning and it was accomplished in three days. The cleaning solutions contained 1.5% citric acid, 1.75% dibasic ammonium citrate, and 1.5% erythorbic acid (1% was used for IPA2). During this cleaning difficulties were encountered in heating the water due to unavailable R.F. power (auxiliary heaters used were much slower). There was inadequate distilled water for the rinses and refills. Plumbing changes being made for other reasons slowed down the cleaning process, and a water leak in the blue purification loop made rinsing difficult. Other tasks at Lualualei have addressed the prevention of corrosion by use of a nitrogen purge system [10,11] and a report details this purge method [12]. In summary, the work done initially at Lualualei was a trial of a simple N₂ sparge in January 1982 and the installation of a more permanent but still simple test system on IPA2 in September of 1982. In March of 1985 and May of 1986 corrosion rates were compared for IPA1 and IPA2 showing considerably less corrosion in IPA2 and confirming the effectiveness of the purge system. The cleaning in April of 1989 showed clearly that less corrosion had taken place in IP A2.

The Annapolis VLF cooling system was cleaned in September of 1986 in a twenty hour period. The tubes were removed for this cleaning and were cleaned separately by hand. The solutions used for the cleaning were 1.5% in citric acid, 1.75% in dibasic ammonium citrate, and 1.0% erythorbic acid. PA1 required four rinses with city water and two with "nuclear grade" water until the resistivity was 600 k Ω -cm. For PA2 four rinses were required to get the resistivity to 220 k Ω -cm. During this cleaning pieces of black rubber were found in the cooling water and baked onto the tube walls, and a coupling was "blown" on the bypass for one of the heat exchangers due to 1 closed valve. The source of the contaminating black material was thought to be gaskets holding the flow sleeves. Although resistivity was adequate when the system was placed back on the purification loop, PA2 did not come up to the expected 1 M Ω -cm level as well as PA1 did. The organic materials added to the water by the rubber caused formation of a slimy film throughout the PA2 system, making cleaning very difficult.

APPLICATION OF THE METHOD

The first step in the cleaning is to determine the necessity for it. Several observations will help in knowing if it is time to do a cleaning. If flow rates of water through the water cooling system decrease it is probable that scale is blocking free flow. This can also be seen if there is a pressure drop of water entering the purification loop. Also if resistivity control becomes difficult and no other cause, such as a leak in the heat exchanger can be found, it may be because oxidation is occurring at a greater rate and oxidation products are fouling the system.

Once it is determined that a cleaning is necessary some precleaning preparation and planning are necessary. These include: 1. site preparation and collection of needed materials; 2. scheduling and time allotment; 3. temperature and concentration choices; 4. planning and arranging for disposal of the solutions from the cleaning. These will each be discussed separately and then a work plan for the actual cleaning can be prepared.

Site Resources

Materials in adequate supply must be on hand before the cleaning commences. Appendix A includes a list of these items. Of special importance is a supply of water for flushing and rinsing. This requires city water and hoses (both fire hoses and garden hoses) of sufficient length to deliver the water to the PA's being cleaned. It also requires enough high purity "nuclear grade" water to flush and rinse each unit as many times as necessary to achieve a resistivity of $>40 \text{ K}\Omega\text{-cm}$. This water can be distilled ahead of time and stored and/or it may be brought in by a distributor. There also must be a way to remove this water from the system quickly to decrease the time it takes to do the cleaning; a pump and fire hoses may be necessary.

Chemicals must also be on hand in adequate supply. Citric acid, $\text{HOC}(\text{CH}_2\text{CO}_2\text{H})_2\text{CO}_2\text{H}$, dibasic ammonium citrate, $(\text{NH}_3)_2(\text{C}_6\text{H}_4\text{O}_7)$, erythorbic acid, $\text{C}_6\text{H}_4\text{O}_6$, and sodium bicarbonate, NaHCO_3 , are needed and they can be purchased in bulk.

Although these chemicals are not toxic, they may be irritating to skin and lungs. It is therefore suggested that protective clothing, such as, gloves and face masks be worn when weighing and mixing these chemicals.

In order to weigh out the chemicals and make transfers, buckets and scoops and a scale are needed. To mix the chemicals into the water a boat oar or paddle which can reach to the bottom of the PA and IPA holding tanks is needed for stirring.

There must also be plugs for the tube sockets so that water can be circulated through the whole cooling loop when the tubes are removed. The tubes themselves can be left in place and cleaned *in situ* or they can be removed and cleaned. If they are removed, a tube holder is needed to hold them in place over a bucket so they can be scrubbed. Scrub brushes are also needed.

In order to circulate the water through the cooling system the operation pumps are usually used. Some plumbing changes may be needed to bypass the heat exchangers or the purification loops and to provide rapid drainage of the cleaning solutions and access to them for testing. It is necessary to heat the cleaning solution to $50\text{-}60^\circ \text{C}$ and this can be done quickly by turning on the transmitter tubes or more slowly, if the transmitter is off, with auxiliary heaters.

To monitor the cleaning as it progresses samples must be removed via drains. Equipment needed to test this water include: a thermometer, a conductivity meter, a pH meter, Cu test kits (0-10 ppm) and O_2 test kits (0-1, 0-40, and 0-12 ppm).

Timing and Time Requirements

Most of the sites have been cleaned in three or four days. Most often a cleaning has been done when the station was scheduled for down time for other maintenance activities. It has been useful for there to be a prior site visit to determine site requirements

Temperature and Concentration

The temperature chosen was $50\text{-}60^\circ \text{C}$. This provides an extra driving force for the dissolution of CuO and makes the cleaning proceed faster. This temperature is most easily reached by turning the transmitter tubes on for a few minutes. If this is not

possible, auxiliary heaters must be used; this is more time consuming.

The solution is made up by first dissolving the citric acid to a concentration of 1.5%(w/w). The dibasic ammonium citrate is then added for a concentration of 1.75%, the pH of the solution is then checked, and more is added if it is needed to raise the pH to 3.5-4.0. This results in a total citrate concentration of about 3.3%. The final addition made is the erythorbic acid. The amount suggested is 2%, but if the system is very clean and the copper concentration is low, then this amount can be reduced to 1-1.5%. Evidence that the erythorbic acid concentration is too high is the formation of a red solid; when this forms the water must be immediately dumped, the system rinsed, and if further cleaning is necessary the cleaning solution is prepared without erythorbic acid.

The cleaning solution is prepared using the water already in the system. The amount of this water is reduced until the minimum needed for circulation is left. An estimate of the volume remaining in the system is then used to calculate the necessary amounts of citric acid, etc. The calculated amounts of the cleaning chemicals are then weighed (amounts in the range of 12- 70 pounds are typical) and mixed in the system tank. Stirring must be done with something, like an oar, which will reach to the bottom of the tank. Once everything is dissolved in the water in the tank, circulation of the solution is begun.

Disposal

Disposal of the cleaning and rinse solutions is site-dependent and is affected by the amount of copper removed, the number of cleanings performed, and the local government disposal regulations and requirements. Generally, the cleaning solutions are transferred to a large holding tank where copper concentration and pH are measured. The solution must then be neutralized with sodium bicarbonate. The resultant solution can then be disposed of in a municipal sewage treatment facility, a shipyard, or if the copper concentration is low (i.e. < 3 ppm), by direct discharge onto the ground. Each site must be evaluated individually and planning must be done before the cleaning.

Procedure

A step-by-step summary of the procedure is in Appendix B.

NITROGEN AND DISSOLVED OXYGEN SYSTEMS

Lamontagne [16] details the complete history of the installation of the nitrogen sparging systems and the dissolved oxygen monitoring systems in this report. The specifications and systems used to maintain a dissolved oxygen concentration below 0.5 ppm and how they are installed at each of the water cooled sites is summarized.

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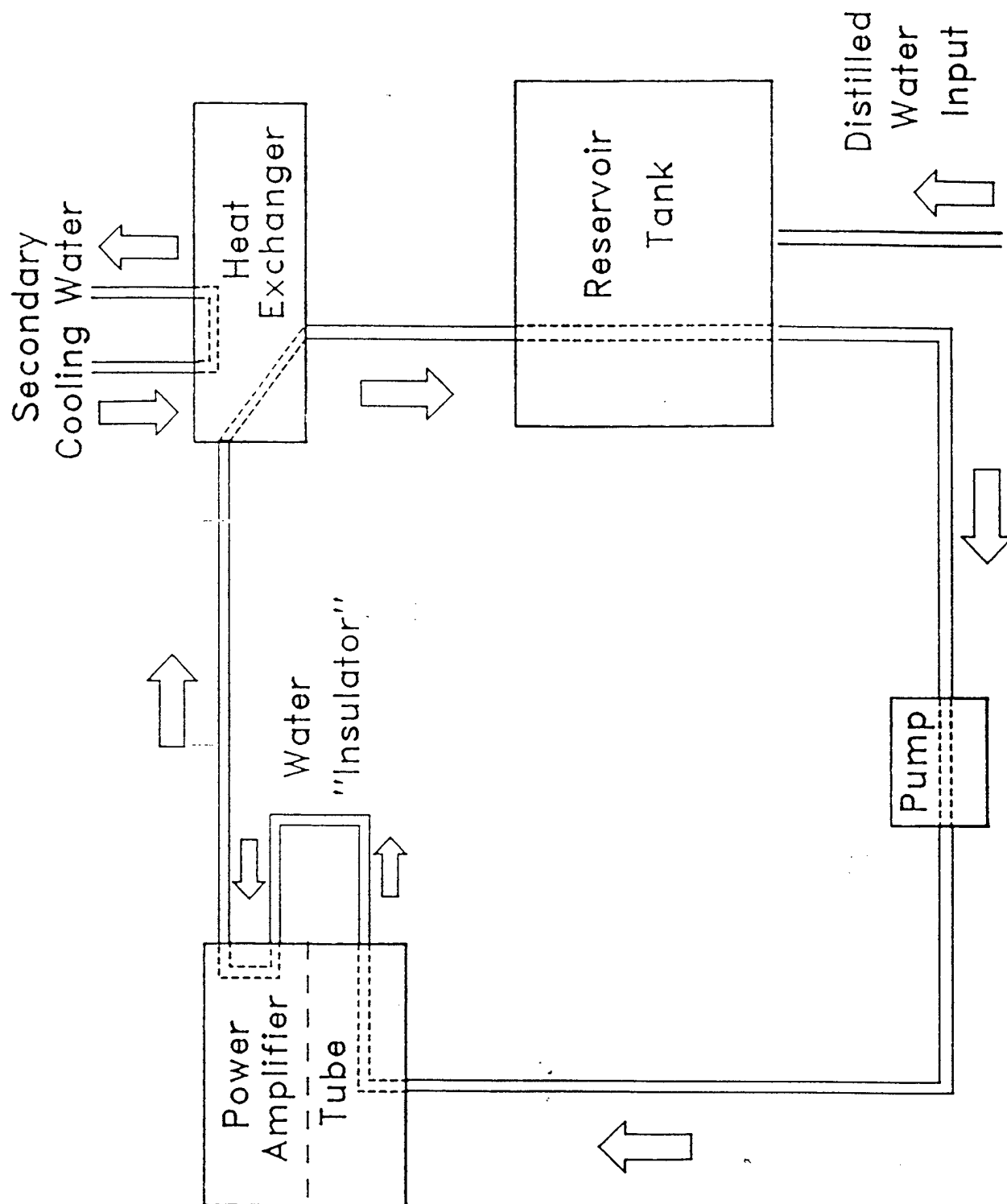


Fig. 1. Portion of a typical VLF transmitter cooling system.

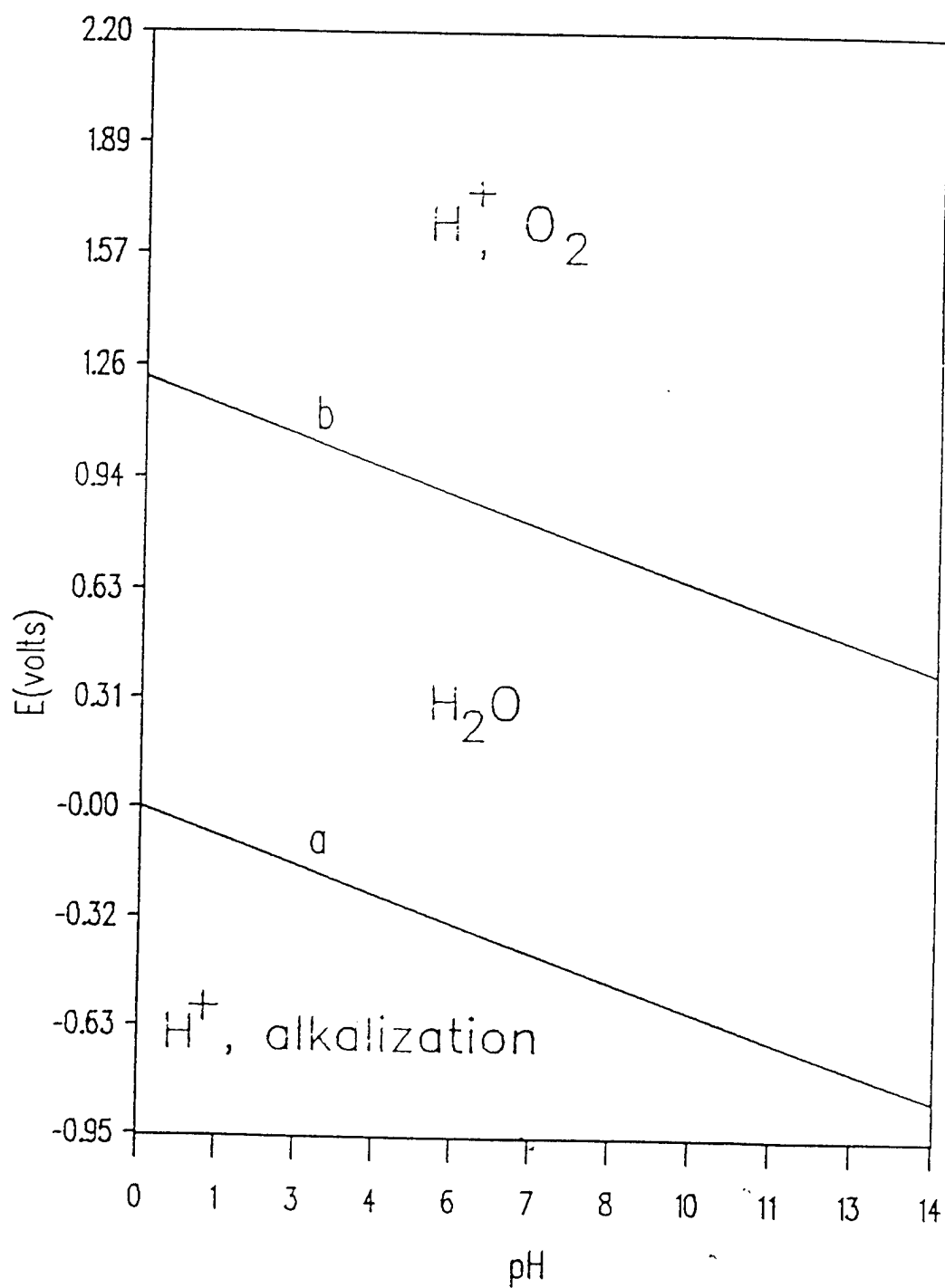


Fig. 2 Pourbaix Diagram For Water

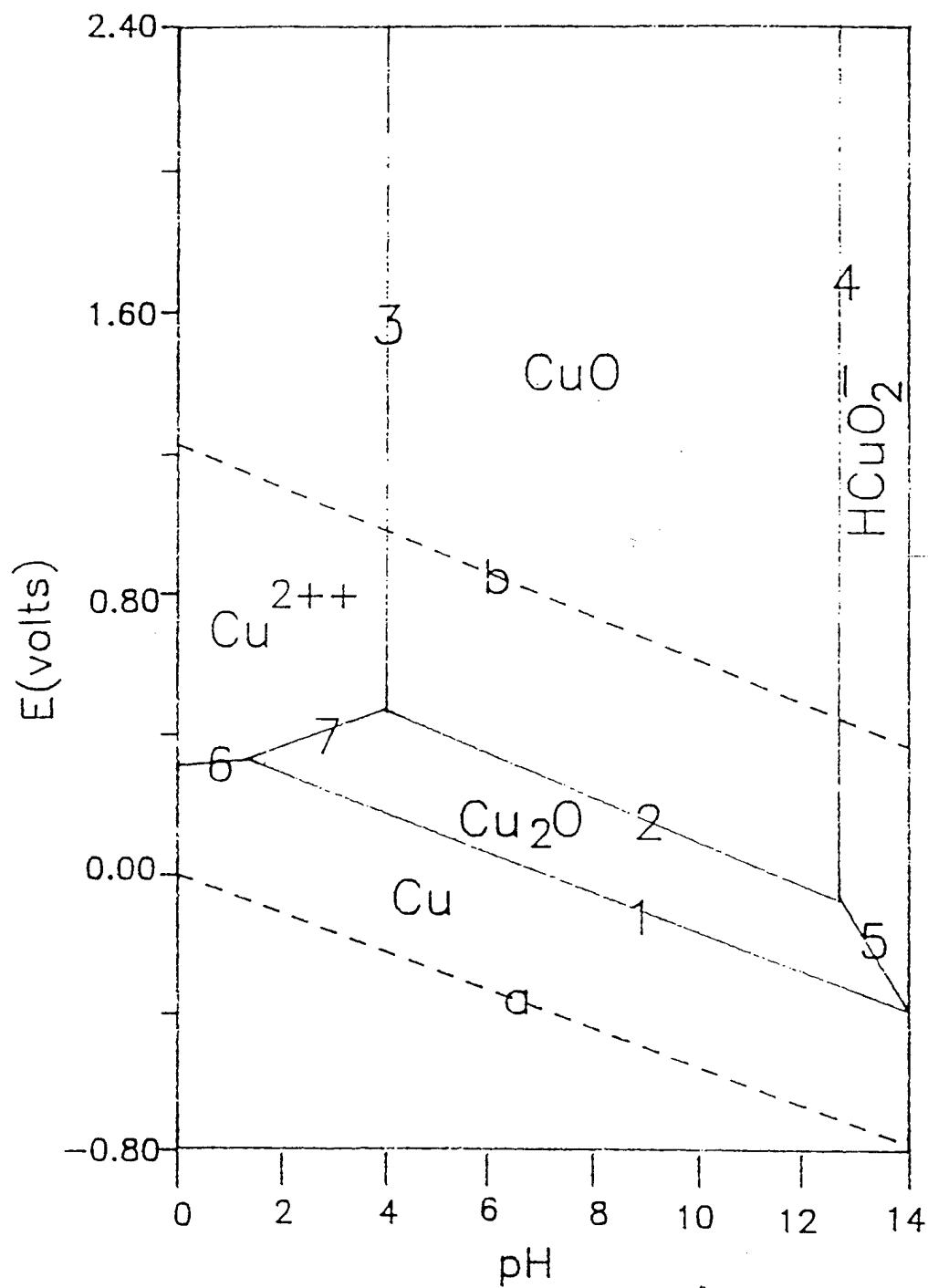


Fig. 3 Pourbaix Diagram for Copper
In Water, Using Equations a, b,
And 1–7 From Text

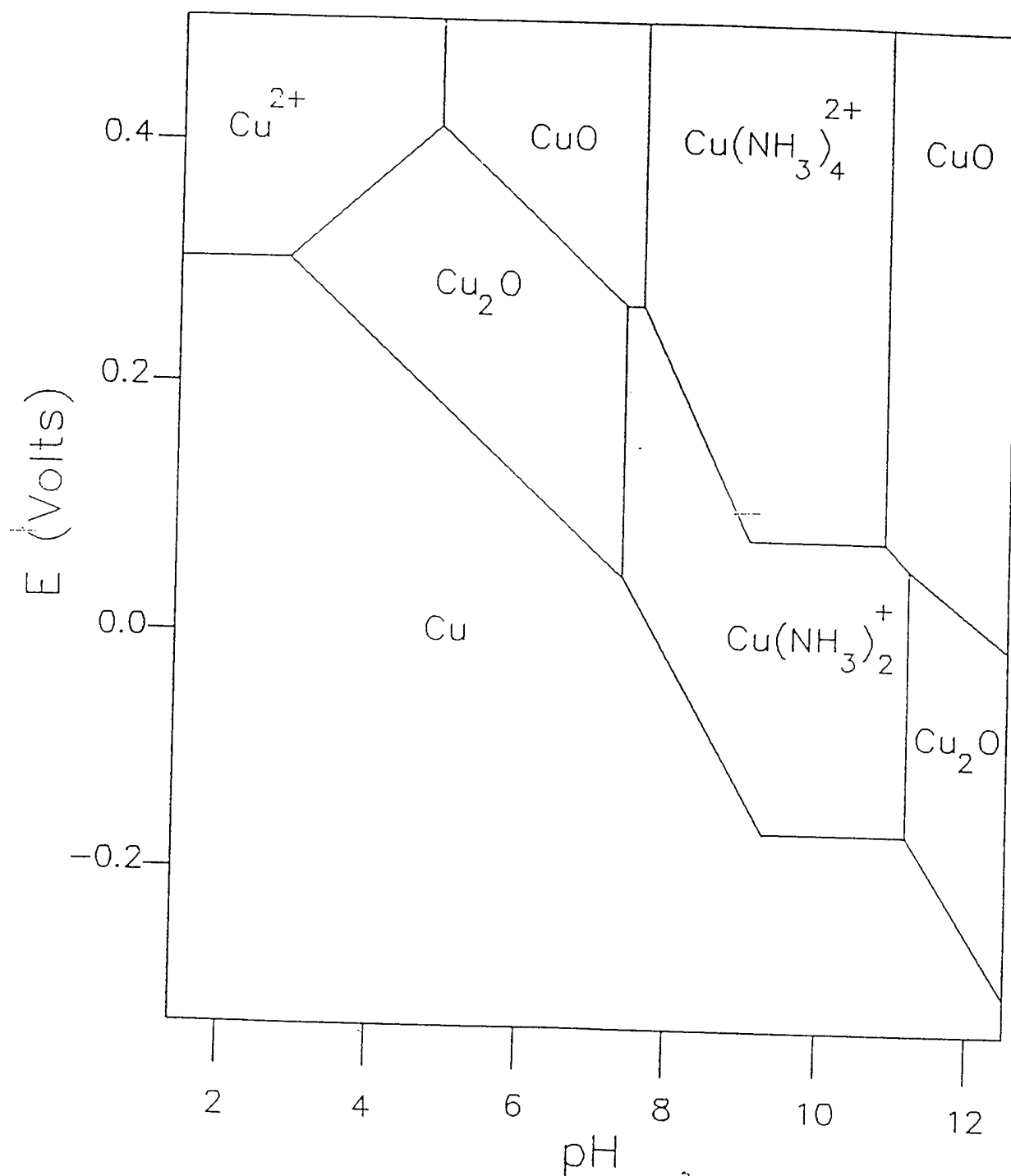


Fig. 4 Pourbaix Diagram For A Copper, Ammonia and Water Mixture

APPENDIX A
ITEMS NEEDED FOR A CLEANING

1. City water and hose
2. Nuclear grade water (in adequate supply) and hoses
3. Pumps to deliver 1 and 2
 - to remove cleaning solutions and flush water
 - and to circulate through the system
 - (self-priming 30-100 gal/min suggested)
4. Hoses to remove cleaning solutions and rinse water to a holding tank
5. Storage/treatment tank for the waste
6. Chemicals: citric acid, ammonium citrate, erythorbic acid, and sodium bicarbonate
7. Balance or scale, buckets, and scoops
8. Boat oar
9. Protective clothing: gloves, goggles, aprons, dust masks
10. Plugs for tube sockets
11. Brushes, sponges
12. Thermometer
13. pH meter
14. Conductivity meter
15. Cu test kits (CHEMet CU-10 or equivalent)
15. O₂ test kits (CHEMet 0-1, CHEMet 0-40, and CHEMet 0-12 or equivalents)

APPENDIX B

STEP-BY-STEP PROCEDURE FOR CLEANING

- I. Close off purification loop and isolate system to be cleaned (check all valves).
2. Reduce water in reservoir tank to 1/3 of original volume (leaving enough to be able to circulate) by transferring to dummy load tank.
3. Heat water to approximately 50°C(122° F).
4. Turn off the heat and stop circulating pumps during the mixing operation.
5. Remove tubes and install tube plugs (this is optional).
6. Add 1.75 % (w/w) dibasic ammonium citrate (calculated based on total volume = reservoir + system plumbing) stirring with oar.
7. When ammonium citrate is dissolved, begin adding 1.5% citric acid to the water with stirring. Measure pH. Adjust pH to 3.5-4.0 by adding more citric acid to lower pH or more ammonium citrate to raise it.
8. When citric acid is dissolved, add erythorbic acid to a concentration of 2%. The amount of erythorbic acid needed is dependent on the amount of copper in the system. If the system is very clean 1% can be used and if a red precipitate of copper appears then no more erythorbic acid should be added.
9. Begin circulating water, turn on heaters, start timing.
10. Circulate 20 to 55 minutes. Monitor [Cu], pH, temperature. The appearance of a green color indicates the cleaning is in progress. If a red color appears, the heaters should be turned off and immediate removal of the cleaning solution and flushing should begin. If a red color never develops, the water should be dumped to a holding tank when the copper concentration levels off or goes above 2000 ppm.
11. Fill the tank with tap water, circulate 10-15 minutes, and drain. Repeat tap water flush at least once, and more if necessary to reduce copper concentration.
12. Visually inspect "clean reservoir tanks". If evidence of debris or CuO build-up remains, drain water and repeat steps 5-10.
13. Flush the system with distilled or nuclear grade water (resistivity $\geq 500 \text{ K}\Omega\text{-cm}$). Circulate for a few minutes (no heat) and drain. Repeat as many times as necessary to achieve resistivity $>40 \text{ K}\Omega\text{-cm}$.
14. When acceptable resistivity is attained, refill system to operation level with distilled or nuclear grade water and put on purification loop.

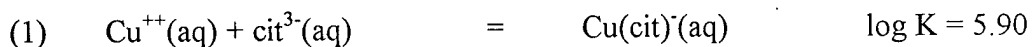
15. The tubes may be cleaned separately using citric acid, rinsed, and replaced in the tube sockets.

16. Personnel measuring and adding chemicals to the tanks should wear a dust mask, gloves, and goggles to avoid prolonged exposure to chemicals (they are non-toxic but can be irritating to lung tissue and skin in some individuals).

APPENDIX C CLEANING CHEMISTRY

The mixture of chemicals used provides three important features to effect the cleaning: the mixture is acidic, there are complexing agents, and there is an antioxidant. The mixture is acidic and is buffered by ammonia so that the pH is in the range 3.5-4.0. Copper oxide is dissolved by acid. This can best be seen in the Pourbaix [C1] diagram in Figure 3 of the text where both reactions 3 and 7 involve the dissolution of copper oxides by the reaction with acid. At pH values lower than 3.5, $\text{Cu}^{++}(\text{aq})$ (or Cu_s) is the dominant species. The cleaning solution avoids reduction of the $\text{Cu}^{++}(\text{aq})$ by providing chelating agents to stabilize the $\text{Cu}^{++}(\text{aq})$. All of the added species, ammonia, citric acid, and erythorbic acid can form Cu(II) complexes. Erythorbic acid also inhibits further corrosion of newly cleaned copper surfaces by reacting with oxygen. This antioxidant also protects other system materials like brass. The complexations will be discussed by first considering the interactions of each ligand separately with $\text{Cu}^{++}(\text{aq})$. The equilibria were calculated using available protonation constants and complex formation constants of a number of copper complexes [C2]. The equilibrium concentrations were calculated by use of the program COMICS [C3]. After looking separately at each cleaning chemical, the analysis of the mixture was done including only those species found to be significant in the previous calculations.

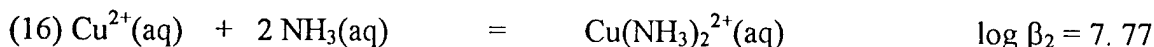
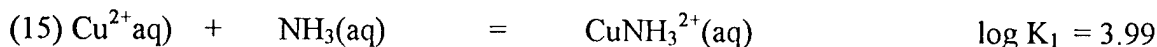
Citric acid is a triprotic acid with structure, $\text{HOC}(\text{CH}_2\text{CO}_2\text{H})_2\text{CO}_2\text{H}$ (see Figure C1). The three acidic groups are carboxylates. The pKa's are 5.68, 4.38, and 2.96. Citric acid complexes Cu^{++} to form many products which differ by the number of citrates, coppers, and protons (or hydroxides). A COMICS routine was run including all of those species which had significant formation constants [C2]. Hydroxide species were not included since the acidic pH of the cleaning solution makes their presence unlikely. From the calculation it is clear that by pH 3 essentially all of the metal is complexed as either $\text{Cu}(\text{cit})^-(\text{aq})$ or $\text{Cu}_2(\text{cit})_2^{2-}(\text{aq})$, and all other copper-citrate species had insignificant concentrations. The formation constants of these reactions which are included in the calculation for the mixture are shown in equations (1) and (2)



Erythorbic acid, EA, is a diprotic acid having pKa's 11.34 and 4.04. Its structure is also shown in Figure C1. It reacts with copper to form two complexes, $\text{Cu}(\text{EA})(\text{aq})$ and $\text{Cu}(\text{EA})_2^{2-}(\text{aq})$ with the formation constants 11.34 and 15.38. In the solution of erythorbic acid and copper, $\text{Cu}(\text{EA})(\text{aq})$ accounts for essentially all of the copper; above pH 8.5 $\text{Cu}(\text{EA})_2^{2-}(\text{aq})$ predominates. Erythorbic acid can also reduce $\text{Cu}^{++}(\text{aq})$ to copper metal. When this happens during a cleaning a red solid is noted and the cleaning solution must be pumped out. Both chelated forms of copper are included in the equilibrium calculation of the cleaning solution, but the electrochemical reaction is not.

Ammonia is a well known copper ligand. The pKa of $\text{NH}_4^+(\text{aq})$ is 9.5. The stepwise formation constants of the reactions of ammonia with copper are $\log K_1 = 3.99$,

$\log \beta_2 = 7.77$, $\log \beta_3 = 10.06$, and $\log \beta_4 = 12.03$ as shown in equations 15-18. If ammonia and copper are the only species in solution the complexation begins at about pH 4 with the formation of $\text{Cu}(\text{NH}_3)^{2+}$ and continues stepwise until pH 7.5 where all of the copper is complexed forming a mixture of $\text{Cu}(\text{NH}_3)_2^{2+}(\text{aq})$ and $\text{Cu}(\text{NH}_3)_3^{2+}(\text{aq})$. By pH 8.5 the predominant form is $\text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$. All of these species were included in the calculation of the mixture.



The equilibria were then calculated using the COMICS routine for the mixture of all of the ligands and the complexes discussed above. The concentrations of the ligands were those added to make the cleaning solution and the copper concentration was that measured in the cleaning solution at Lualualei. The results of this calculation are best summarized by the plot in Figure C2 which shows the dominant forms of copper in the pH range 3-6 to be $\text{Cu}(\text{cit})^-(\text{aq})$, $\text{Cu}_2(\text{cit})_2^{2-}(\text{aq})$, and $\text{Cu}(\text{EA})(\text{aq})$. Between pH 7 and 8, $\text{Cu}(\text{EA})_2^{2-}(\text{aq})$ is also becoming significant. Above pH 3 there is essentially no free copper in solution. The cleaning solution does turn green as expected from the formation of the copper-citrate complexes.

The cleaning process can thus be summarized as the acid dissolution of copper(II) oxide to form $\text{Cu}^{++}(\text{aq})$, which is then complexed by citric or erythorbic acid. The erythorbic acid also reacts with oxygen to protect copper metal and brass from further corrosion.

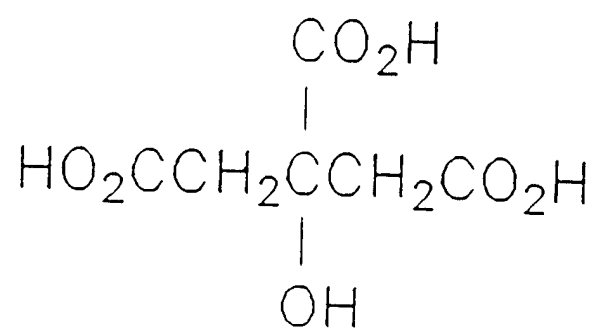
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(a) citric acid



(b) erythorbic acid

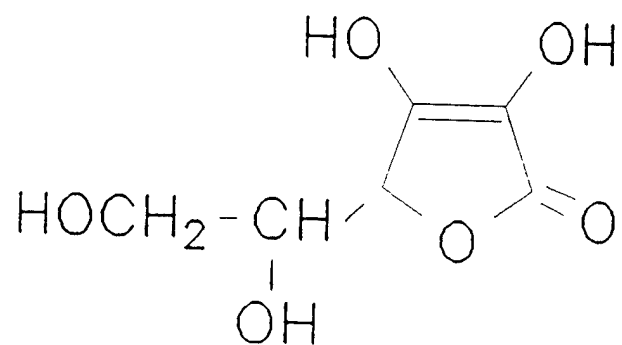


Fig. C1 Structures of
Cleaning Chemicals

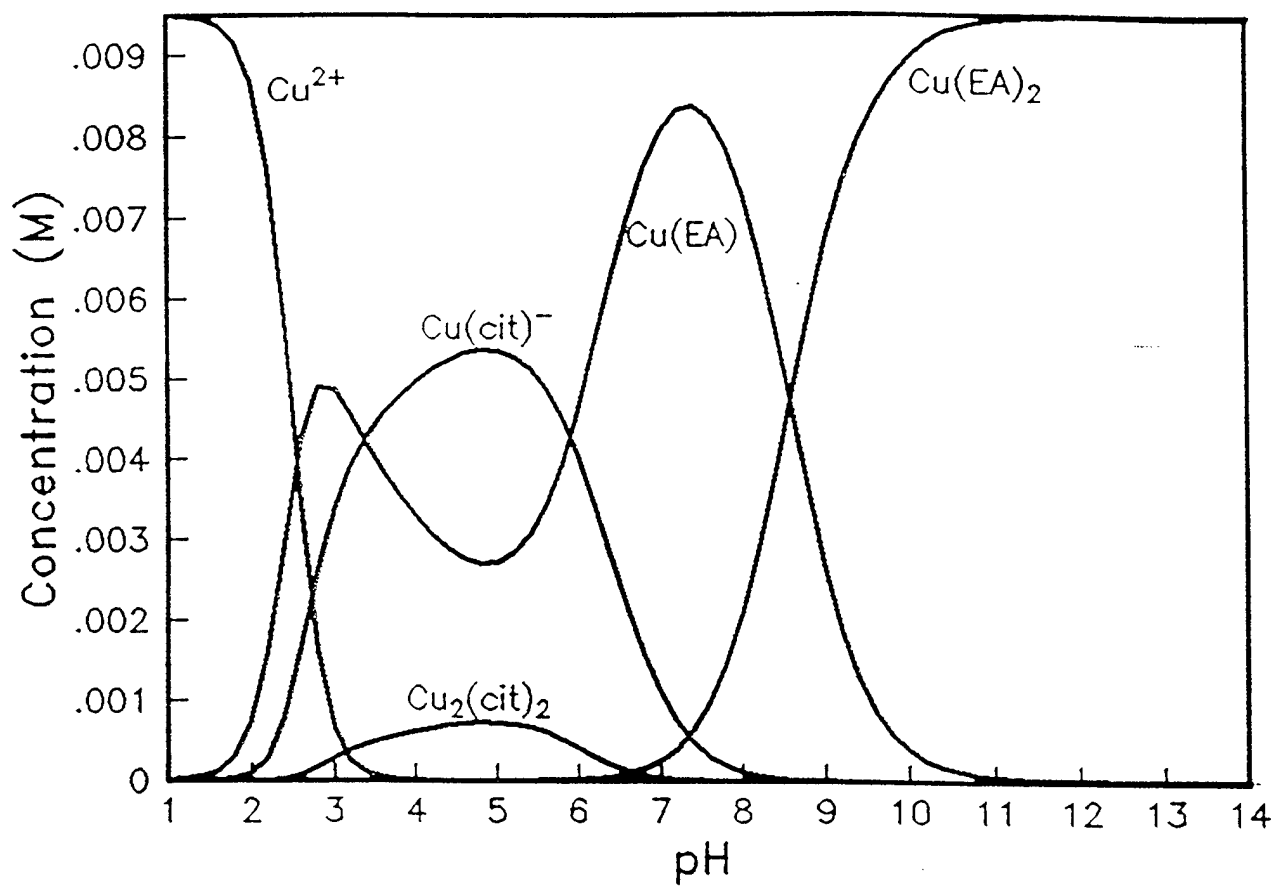


Fig.C2 Significant Copper Species
in Cleaning Solution